

**A Submonolayer of Pt on Ru Nanoparticles - A Low Loading High CO Tolerance Electrocatalyst**

S.R. Brankovic, J.X. Wang, R.R. Adzic

Energy Sciences and Technology Department  
Brookhaven National Laboratory  
Upton, NY 11973

Recent research activity to improve Pt-Ru electrocatalysts for the oxidation of reformat  $H_2$  containing a small concentration of CO has been stimulated by development of fuel cells for electric vehicles, an area that is currently gaining considerable momentum. It is generally believed that Ru facilitates CO oxidation on Pt through the bifunctional mechanism. It is also believed that the electronic effects can be operative whereby the interaction of Pt with Ru weakens its bonding with CO. To clarify the extent of the role of the bifunctional mechanism and the electronic effect, and to improve the performance of the Pt-Ru electrocatalysts we focused on a characterization of well-prepared Ru single crystal surfaces and exploration of controlled deposition of Pt thin layers on Ru(0001). This work demonstrated that spontaneous deposition of Pt on Ru can occur and can yield monolayer-to-multilayer deposits.

The spontaneous deposition of Pt established with Ru(0001) can be used to tailor active, low Pt loading electrocatalysts on metallic Ru nanoparticles. This method facilitates a deposition of Pt only at the surface of Ru nanoparticles rather than having Pt throughout the nanoparticle as in the Pt-Ru alloys. Ru nanoparticles with submonolayer Pt islands of monolayer-height may provide active catalysts since the remaining Ru surface acts as an oxygen supplier for the oxidative removal of CO. In contrast to the Pt-Ru alloy nanoparticle catalysts this structure has all the Pt atoms at the surface available for the catalytic reaction. At the same time, all the Pt atoms are in direct contact with Ru atoms, which facilitates a strong electronic interaction between Pt and Ru atoms and, hence, a strong reduction of the CO adsorption energy on Pt. In addition, by placing a catalyst in the surface region, rather than throughout the nanoparticle, a considerable decrease of a Pt loading is achieved.

Fig. 1 shows the morphologies of two Pt deposits on a well ordered Ru(0001). The Pt deposit obtained from a 0.1mM  $H_2PtCl_6$  + 0.1 M  $H_2SO_4$  solution for 2 minutes consists of a great number of Pt clusters which have a columnar shape and a relatively uniform size. Their height is in the range of 3 to 5 nm (10-15 ML) and their diameter is between 6-10 nm (Fig. 2). The total amount of Pt deposited is between 4 and 5 ML. The Pt deposit obtained from the 10mM  $H_2PtCl_6$  in 0.1 M  $H_2SO_4$  solution during one minute is shown in the right image. The entire Ru surface is covered with 2-6 nm-sized clusters with an average height of 2 ML. About 92 % of the Ru surface is covered and the total amount of deposited Pt is approximately ~2 ML. The mechanism of this deposition is not entirely clear, in particular a multiplayer deposition of Pt. It is likely that the Ru surface oxide formation supplies the electrons for the reduction of Pt ions.

Rotating disc electrode measurements with catalysts deposited on a glassy carbon electrode and covered by a thin Nafion® layer, have been used for determination of their activity and CO tolerance. Although this method has been described in several publications, a detailed comparison of the activity of

various catalysts requires a careful evaluation of the adequate comparison conditions. We have demonstrated that a determination of the  $H_2$  oxidation kinetic current as a function of catalyst loading can be used for identification of the catalyst layer thickness that facilitates its optimal utilization. The measurements of CO tolerance for that particular thickness provide a reliable comparison of different electrocatalysts.

Fig. 2 (upper panel) shows a Pt mass – normalized currents obtained at 0.05V with rotating thin catalyst layer disk electrode for  $H_2$  oxidation as a function of rotation rate for the electrocatalysts obtained by spontaneous deposition of Pt on Ru nanoparticles on Vulcan XC72 and for E-TEK's 20% 1:1 PtRu electrocatalyst. Kinetic  $H_2$  oxidation currents are indicated in the graph. Lower panel shows a time dependence of the currents at 0.05V for the oxidation of  $H_2$  with 1000ppm of CO, normalized by the current in the absence of CO for the respective catalyst. The CO tolerance of the new electrocatalyst is considerably higher than that of the commercial sample.

Further efforts in the application of this novel catalysts preparation method and the optimization of Pt coverage on Ru nanoparticles will be presented.

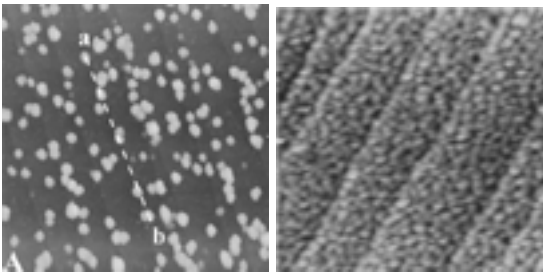


Fig. 1 STM images (200 x 200 nm, left and 100 x 100 nm, right) of spontaneously deposited Pt on Ru(0001) from solutions containing 0.1mM and 10mM  $H_2PtCl_6$  in 0.1M  $H_2SO_4$ , respectively. Images recorded at open circuit potentials with Z ranges 5nm (left) and 2nm (right).

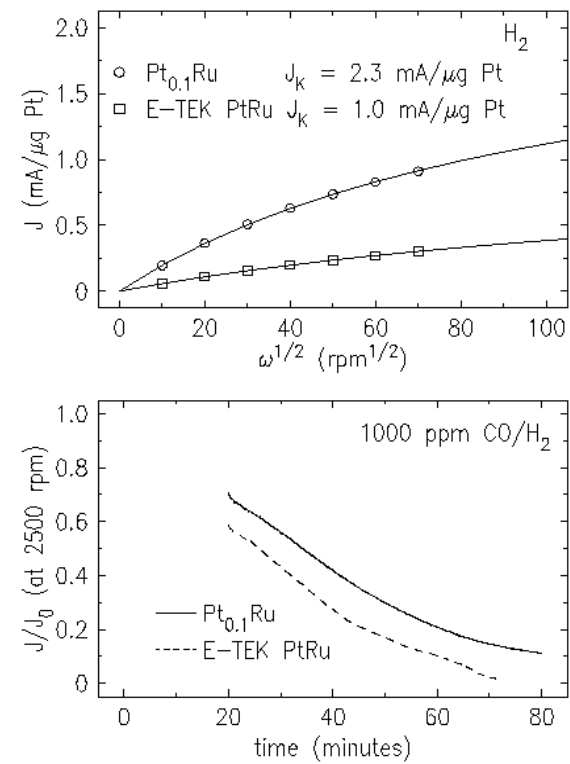


Fig. 2 Comparison of the catalyst prepared by spontaneous deposition of Pt on Ru nanoparticles on Vulcan XC72 and of E-TEK's 20% 1:1 PtRu catalyst for the oxidation of  $H_2$  and  $H_2$  with 1000ppm CO at 0.05V in 0.5M  $H_2SO_4$ . 25° C, 2500rpm, disk area: 0.2 cm<sup>2</sup>.